

Understanding Protective Film Formation on Magnesium Alloys in Automotive Applications

P.I. M.P. Brady

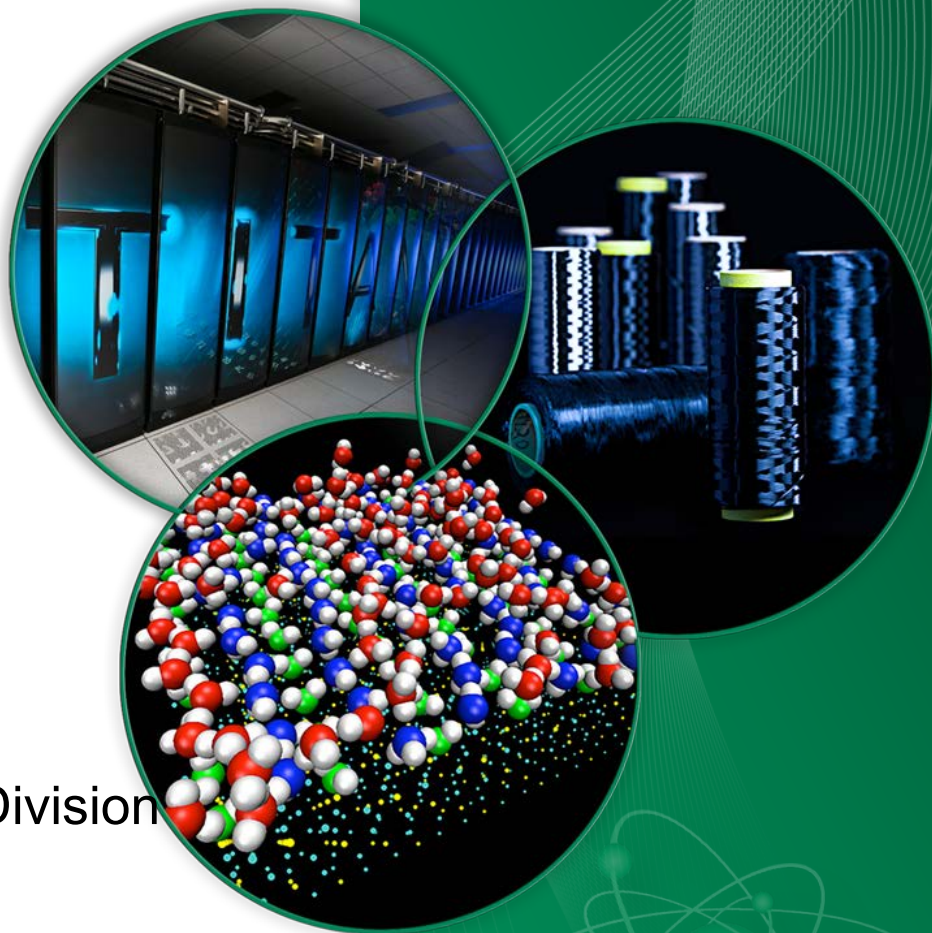
Co-P.I. K.A. Unocic

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Project ID #
LM076

Overview: Project

Timeline

- Project start: Feb. 2012
- Project end: Sept. 2015
- ~65 Percent complete

Budget

- Total project funding
 - \$1350k DOE share
 - \$210k In-Kind (MENA)
- \$300k received in FY13
- \$450k in FY14
(PI cost per year ~ \$400k)

Barriers

- Barriers addressed
 - Lightweight Materials Barrier H: Maintenance, Repair, and Recycling
 - Lightweight Materials Barrier C: Performance (corrosion resistance)
 - 50% vehicle body/chassis weight reduction target will require low-cost, corrosion-resistant Mg alloys

Partners

- Magnesium Elektron North America (MENA)
- University of Manitoba (collaborator)
- Project Lead: Oak Ridge National Lab

Relevance: Develop Scientific Foundation for Mg Alloys w/ Improved Corrosion Resistance

- Mg and carbon fiber have the highest potential to achieve targeted 50% weight reduction in vehicle body and chassis
- Mg alloys need to enable recycling, low cost joining, and corrosion resistance for successful implementation
- Must achieve this with reduction or elimination of rare earth additions
- Film formation and corrosion of Mg is highly complex
 - Improved scientific understanding needed to provide the basis to develop more corrosion-resistant Mg alloys and coatings
 - Focus on how alloy additions to Mg affect structure, chemistry and protectiveness of film formation (bare alloys and conversion coatings)

Milestones Focus on New Film Characterization Techniques and Findings Dissemination

- ✓ **FY 2013** Determine feasibility to perform isotopic tracer studies (^{18}O , ^2H) for Mg corrosion (8/31/2013): **Go Decision for this approach**
- ✓ **FY 2013** Submit at least one journal article on Mg alloy film growth based on down selected advanced characterization technique findings (9/30/2013): **MET- JES Paper on TEM study of films grown in water**
- ✓ **FY 2014** Determine feasibility of measuring impacts of nanoscale porosity and/or H species incorporation into Mg corrosion products by SANS. (12/31/2013): **Go Decision for this approach**
- ✓ **FY 2014** Complete baseline isotopic tracer study of film growth in water (3/31/14): **Met- Paper submitted**
- ✓ **FY 2014** Determine feasibility of 3D Mg corrosion atomic scale chemistry by atom probe tomography (6/30/14): **No go decision.**
- ✓ **FY 2014** Submit paper on advanced characterization study of salt species effects on surface film (9/30/2014): **On Track**

Strategy: New Advanced Characterization Techniques to Elucidate Film Formation

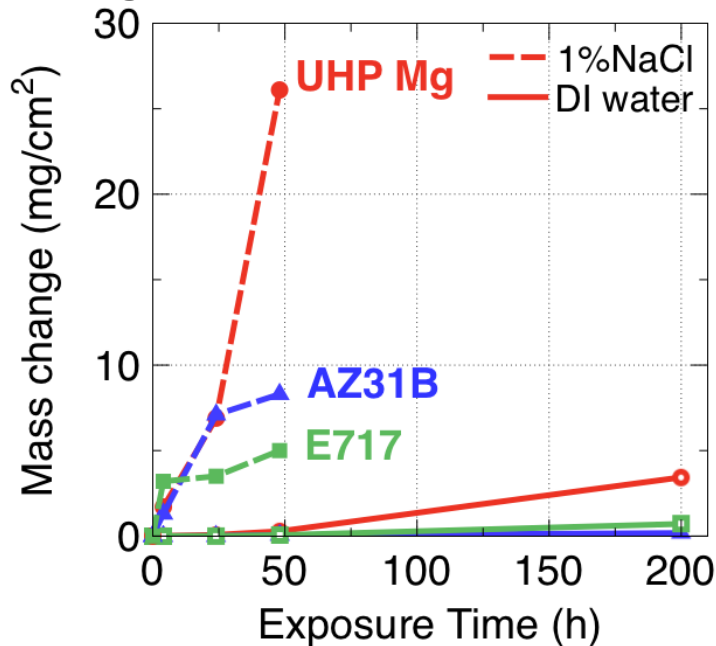
- Film formation on bare Mg alloys and conversion coatings are one key to corrosion resistance
- Near-ambient films on Mg relatively thick
 - Tens of nanometers to microns as opposed to thin ($< 10\text{nm}$) films formed on stainless steels, Al, etc.
 - Shares characteristics with films more often observed for heat-resistant alloys in high-temperature oxidation and corrosion
- Apply new characterization techniques from high-temperature oxidation to ambient films on Mg
 - Cross-section transmission electron microscopy (TEM)
 - Isotopic film growth mechanism tracer studies with D_2O and H_2^{18}O
 - Small angle neutron scattering (SANS) of Mg film structure/nanoporosity
 - Combine with established surface chemistry + electrochemical approaches

Strategy: Focus on How Alloy Chemistry and Exposure Affect Surface Film Structure, Chemistry, and Protectiveness

- Demonstrate new characterization techniques and insights for ambient aqueous film formation \pm salt
 - Goal is not corrosion rate assessments, such data already available
 - Short term (4-48 h) immersion studies + multiple technique characterization to understand initial film structure, chemistry, and growth mechanism
 - Complement immersions with electrochemical studies
- In-depth focus on AZ31B and E717: Represents two major vehicle relevant Mg alloy classes (both near-single phase)
 - **AZ31B**: Mg-(2.5-3.5)Al-(0.7-1.3)Zn-(0.2-1)Mn wt. %
 - **Elektron 717**: ZE10A type with Mg-(0.7-1.3)Zn-0.25Zr-(<0.5)Nd wt. %
(successful warm forming of door panels from E717 reported, Niu et al., Cosma, Thermec 2013)
 - Compare film growth w/pure Mg and model alloys for control purposes
- Compare film formation on bare vs. coated AZ31B and E717
 - Alodine® 5200 and Surtec® 650 \pm BASF 525 E-coat (selected by MENA)

Project Stage Moving From Pure Water Exposures to Water + Salt

100x Higher Mass Gains in Salt Water



FY 14: H₂O + NaCl Exposures

- ~100x higher mass gains in 1% NaCl than in pure water
- Alloys show greater resistance in 1% NaCl than the pure Mg studied
- TEM + SANS in-progress focus to understand how NaCl degrades film - build on and compare with baseline pure water exposures
- FY14/15: Bare metal water ± salt studies as baseline for same alloys with conversion coatings ± E-coat

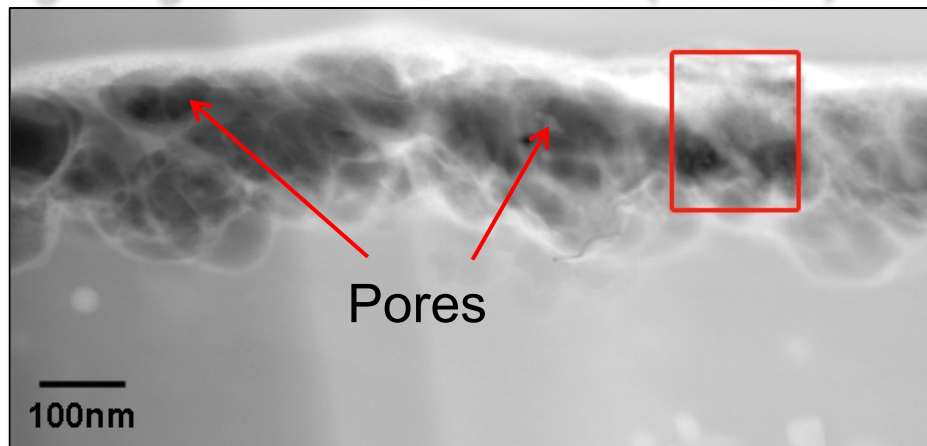
FY 13: Pure H₂O Exposures

- Thinner films/reduced corrosion for alloys compared to pure Mg
- Water film analysis as base for comparison with NaCl exposures
- FY 14: tracer studies in water

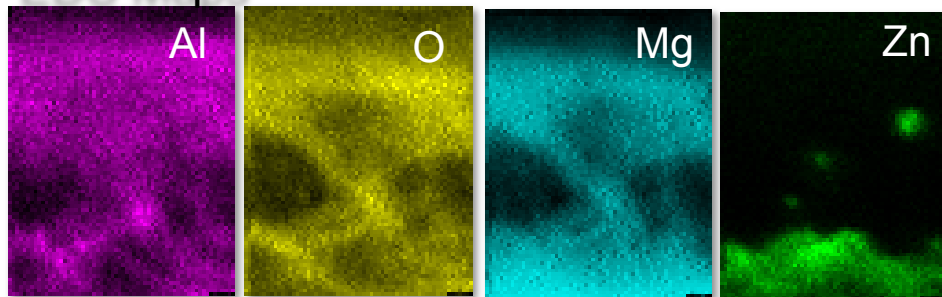
FY13: Al in MgO-base Film and Zn at Film-Metal Interface for Water Exposed AZ31B

Cross-Section TEM and Elemental Maps for AZ31B After 24 h in H₂O

High Angle Annular Dark Field (HAADF) Image



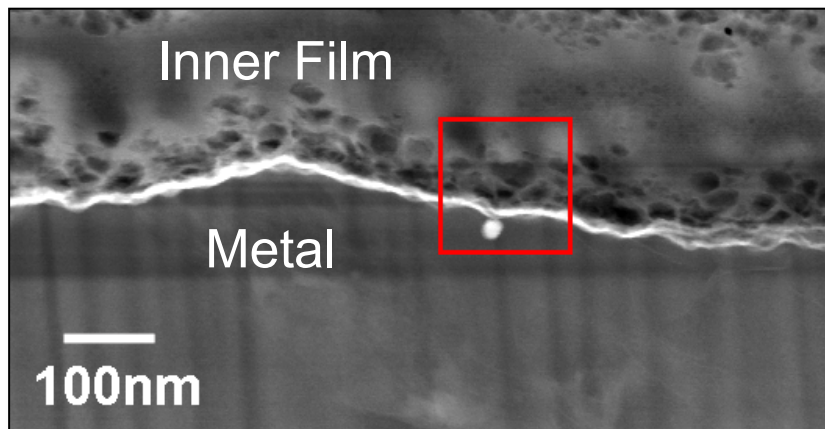
EDS Maps



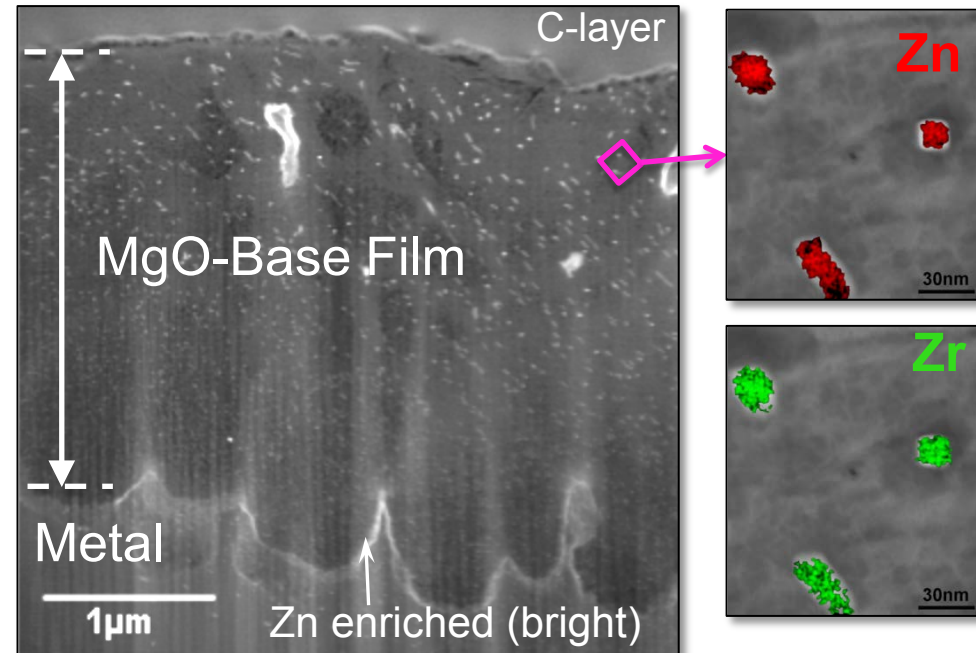
- MgO enriched with Al
- XPS indicates Al present in oxidized state, likely dissolved in MgO
- TEM data indicates Zn enriched in metal form at film-metal interface
- Also, Zn-rich precipitates in the film

FY13: Zn and Local Nd Enrichment at Film-Metal Interface for Water Exposed E717

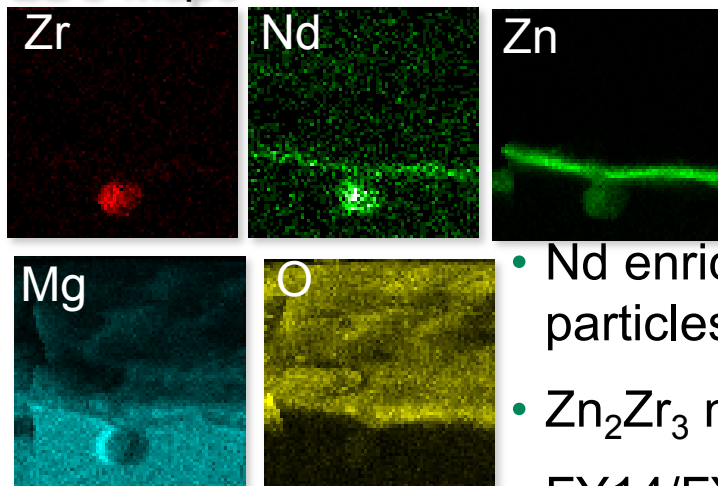
After 24h in H₂O



After 48h in H₂O



EDS Maps



- Nd enrichment only in local regions near where Nd-Zr alloy particles present (*beneficial?*)
- Zn₂Zr₃ nano particles in growing film (*beneficial?*)
- FY14/FY15: E717 with different particle distributions and model versions Zn Nd/Ce under study

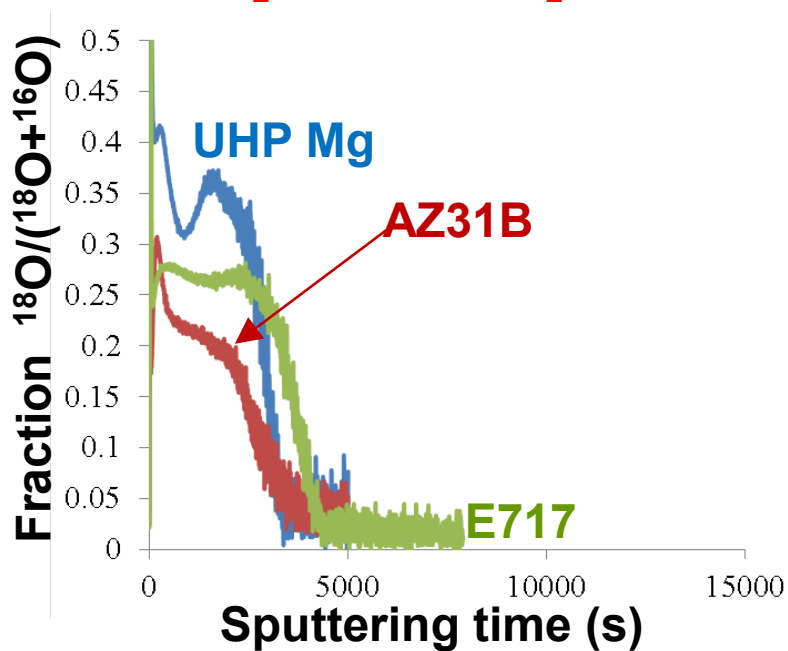
FY14: Successful SIMS Isotopic Tracer Studies for Mg Film Formation in Water

- Approach used in high-temperature alloy oxidation studies, not previously applied to corrosion films on Mg
- Conducted for UHP Mg, AZ31B, and E717
- Tracer waters containing $^{18}\text{O}/^{16}\text{O}$ or H/D used individually and/or sequentially for new insights into film growth by Mg in water
- Exposure conditions guided by previous TEM and XPS findings
 - 4 h D_2O
 - 4 h ^{18}O water
 - 4 h D_2O + 20 h ^{18}O water
 - 4 h ^{18}O water + 20 h D_2O
 - 80°C humid air: 4 h ^{18}O water + 20 h D_2O
- Extensive data set (1 highlight shown in following slide)

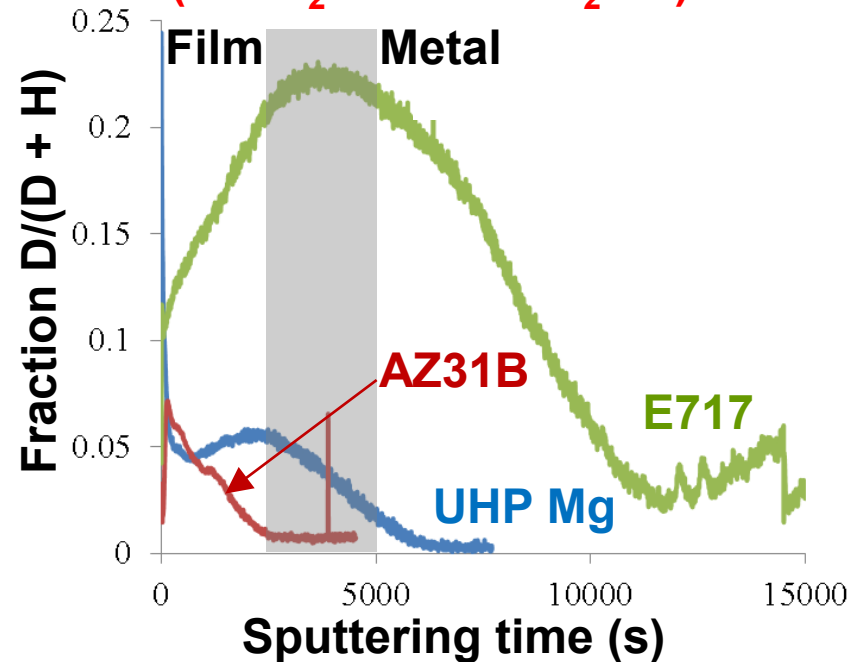
FY14: Major Differences Among Alloys in Film Growth and Hydrogen (D) Penetration in Water

SIMS Sputter Data from Film Surface to Underlying Metal

^{18}O Fraction vs. Film Depth
(4h D_2^{16}O + 20h $^{1}\text{H}_2^{18}\text{O}$)



D Fraction vs. Film Depth
(4h $^{1}\text{H}_2^{18}\text{O}$ + 20h D_2^{16}O)



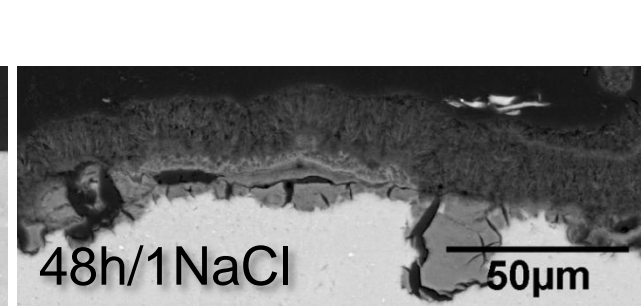
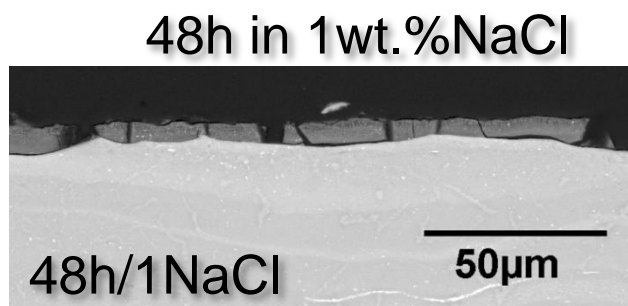
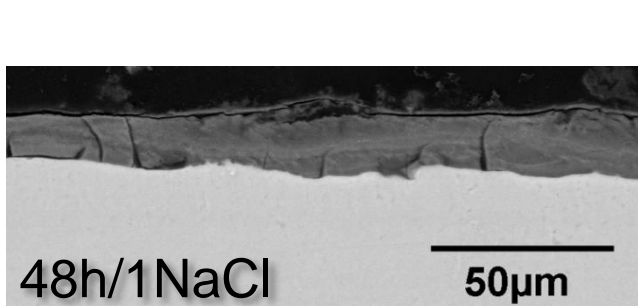
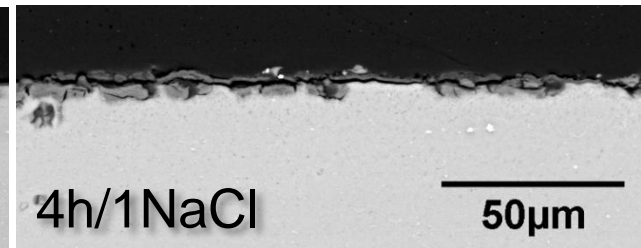
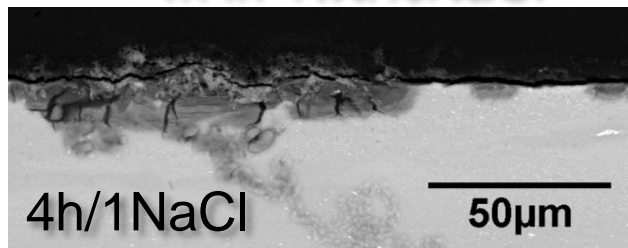
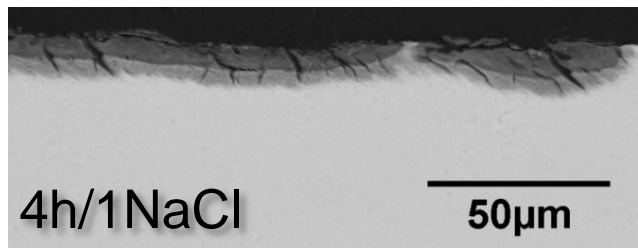
- Extensive D penetration in E717 beyond film into underlying metal
- UHP Mg likely mixed metal outward + D/O inward growth (“dips” in data)
- AZ31B and E717 inward D/O growth, short circuit D inward for E717

FY14: SEM Cross-Sections Show Far Thicker Films After Exposure in 1% NaCl vs. Pure Water

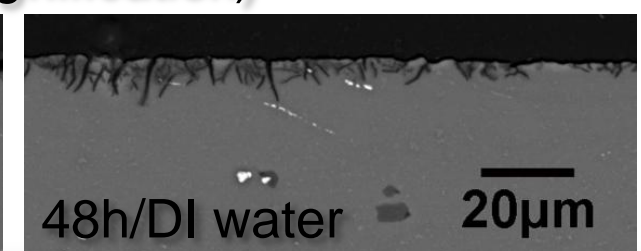
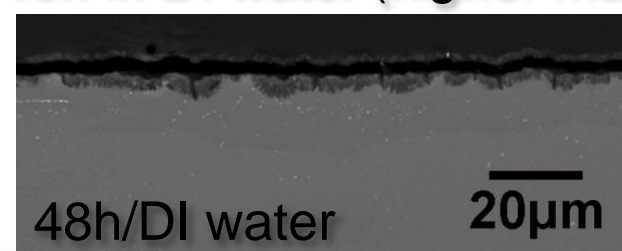
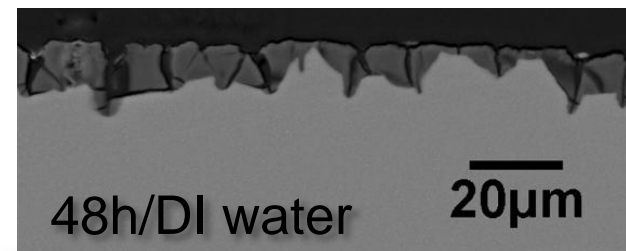
UHP Mg

E717
4h in 1wt.%NaCl

AZ31B

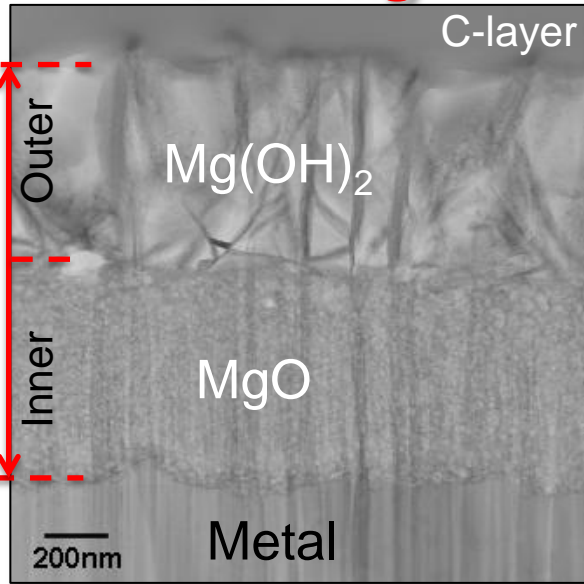


48h in DI water (*higher magnification*)

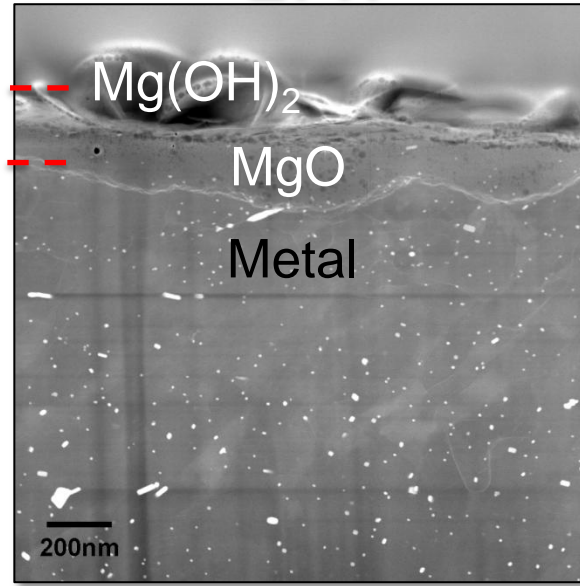


FY14:TEM Cross-Sections Show Thicker, Porous $\text{Mg}(\text{OH})_2$ After 4h in 1%NaCl vs. Water

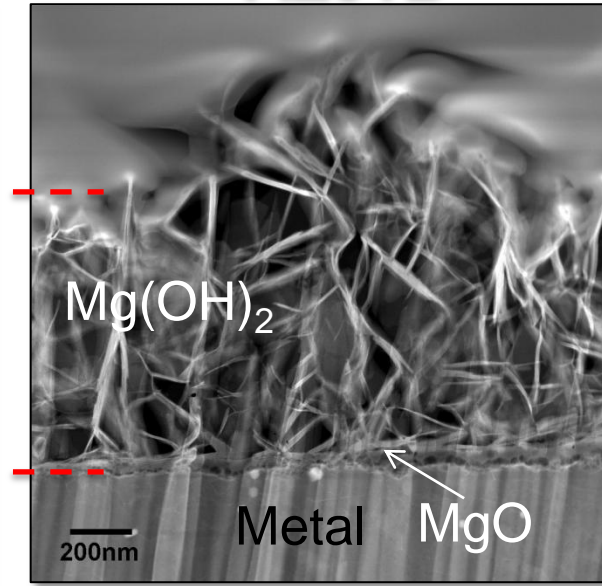
UHP Mg



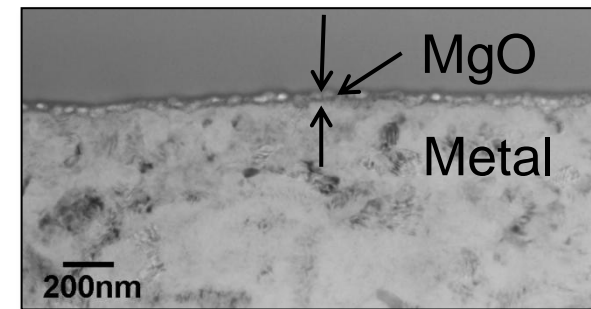
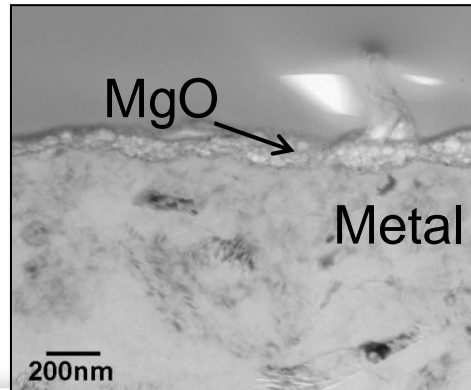
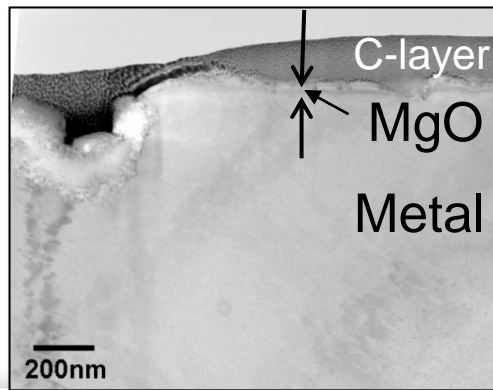
E717



AZ31B

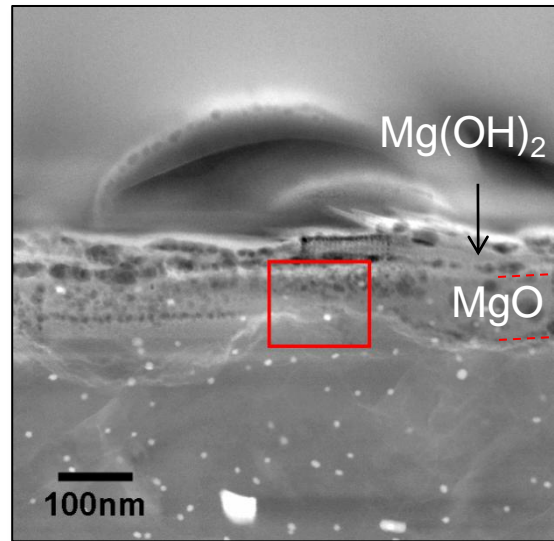


4h in DI water



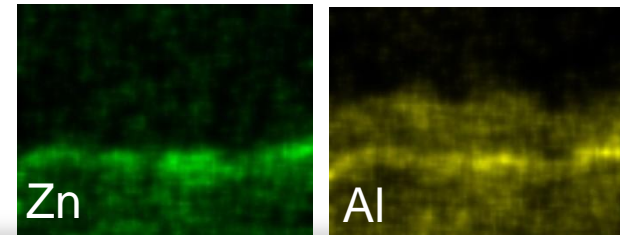
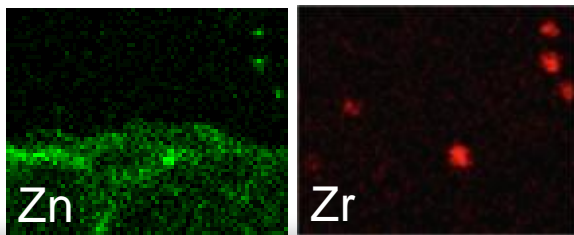
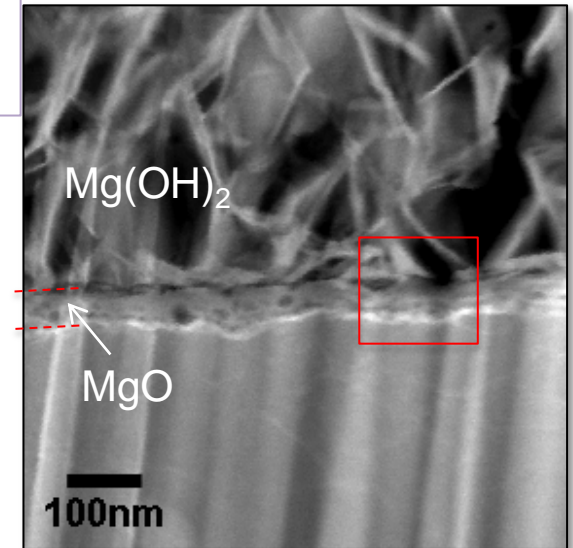
FY14: 4 h 1%NaCl: Zn_2Zr_3 Precipitates in E717 and Al in AZ31B Only in Inner MgO Layer

E717



Cl found in inner layer
Zn at the metal/film interface
(but less continuous than in H₂O)

AZ31B



FY14: Small Angle Neutron Scattering of Bare and Coated Mg Alloys in Water \pm NaCl

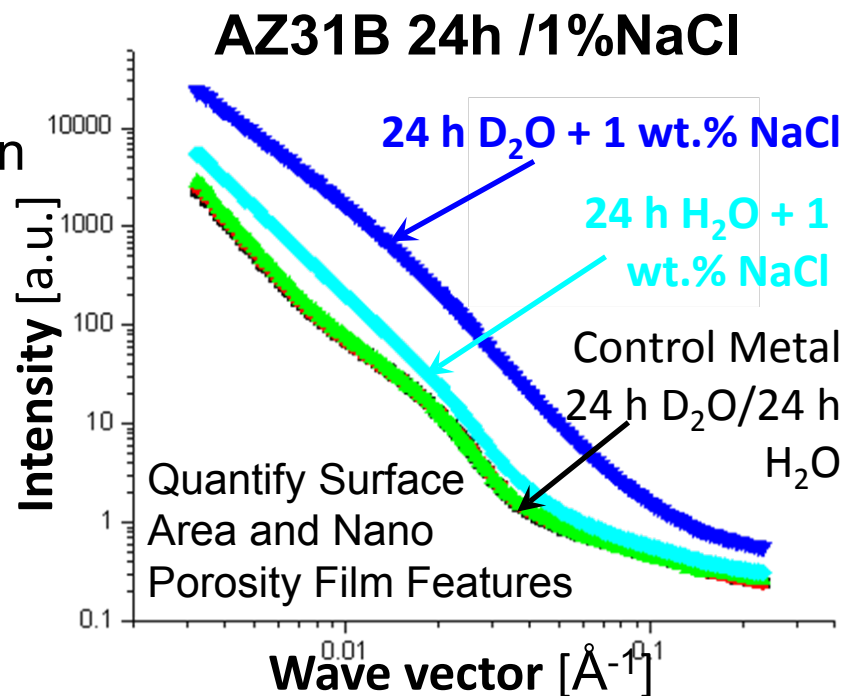
- SANS can quantify entire sample volume
 - Insights for nanoscale porosity, precipitates, and potentially H segregation

- Bare metal (AZ31B and E717) and as-coated (analysis in progress on coated with conversion coatings) (planned future work on e-coat top coats)

- 24 h $\text{H}_2\text{O} \pm 1$ wt.% NaCl
- 24 h $\text{D}_2\text{O} \pm 1$ wt.% NaCl

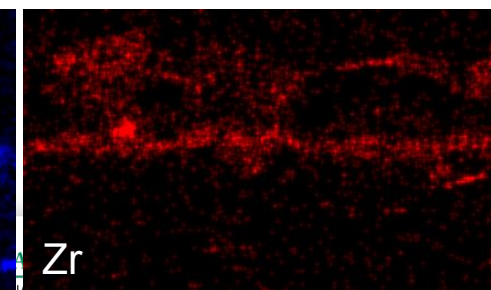
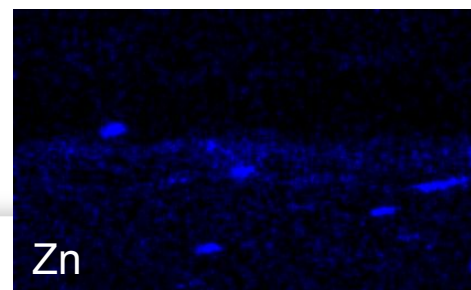
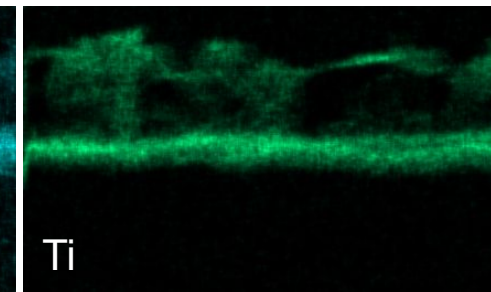
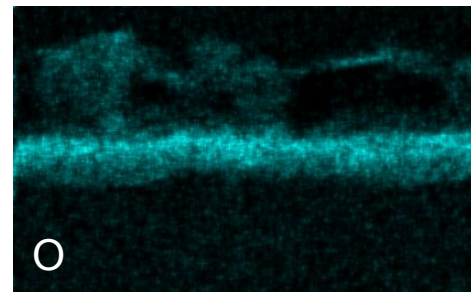
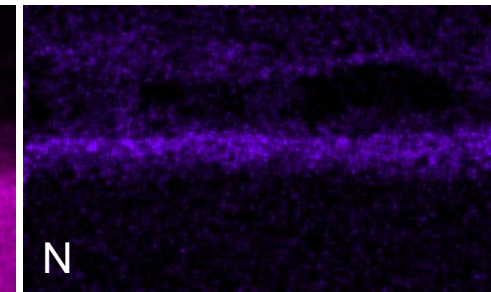
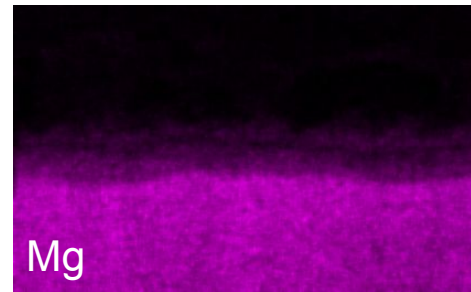
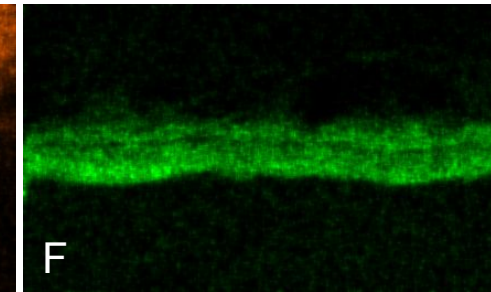
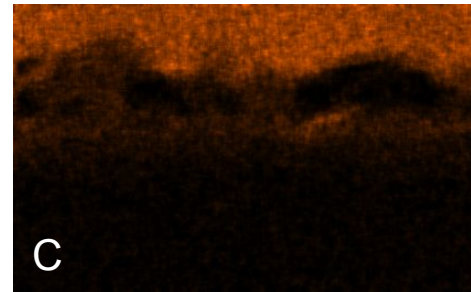
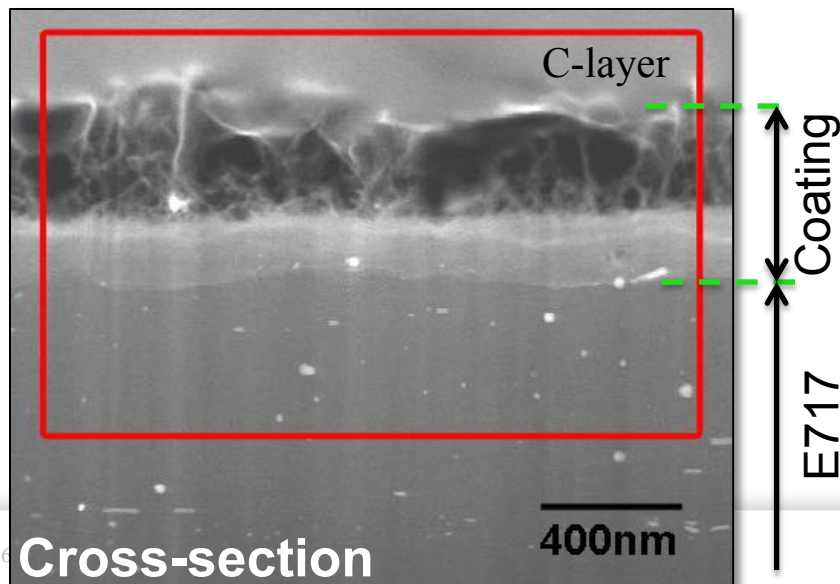
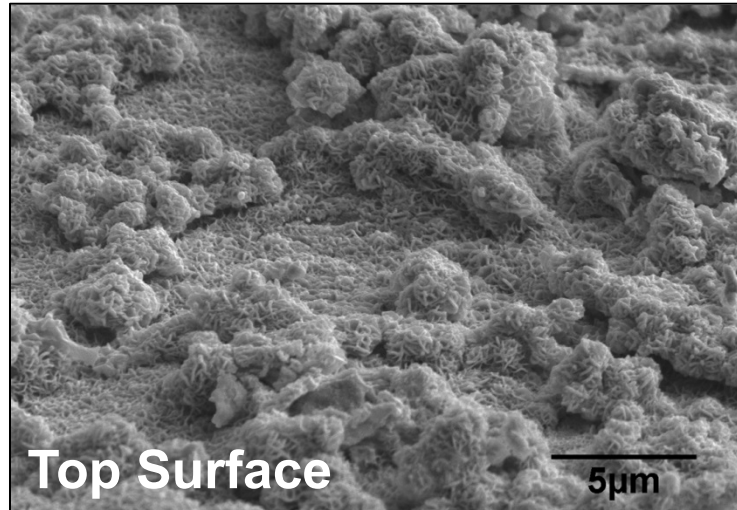
- Extensive data set (1 example shown)

- Films in pure water don't alter scattering relative to unexposed metal
- Films formed in 1 wt.% NaCl modify scattering: porous $\text{Mg}(\text{OH})_2$ layer
- Using D_2O helps accentuate scattering of porous $\text{Mg}(\text{OH})_2$ in 1 wt.% NaCl



FY14: TEM Studies of Conversion Coatings Successfully Initiated

As-Coated Alodine® 5200 on E717



Response to Reviewer Comments

Recognition of unique characterization efforts for Mg corrosion surface films, but comments regarding need to study as-received, non corroded surfaces and fully characterize alloy grain size, structure, impurities, etc.

Due to limited time and review slide format we can only highlight aspects of our results, but unfortunately cannot go into such detail. We had/have XPS, SANS, and SIMS data for as-prepared surfaces prior to corrosion as well as grain size analysis and impurity contents for all materials studied. We also are obtaining as-coated XPS, SANS, and TEM for control prior to corrosion (same alloy sets for bare and coated).

Comments, concerns, and suggestions for project vision and focus.

There are a large number of excellent galvanic and electrochemical studies of Mg corrosion, but nano/micro details of segregation of alloy/coating elements to the surface films that impact corrosion resistance are lacking. Our vision is to demonstrate new approaches by detailed study of relevant Al (AZ31B) and RE (E717) type alloy classes (with supporting model alloys), both bare and coated, and in water and salt. These approaches can then be adopted by other groups to a wide range of wrought and cast Mg corrosion issues. Assessment of new techniques for Mg alloys is a major/costly endeavor. Expansion to many other alloy types (die cast grades, comparative Al alloys) or phenomena (galvanic and grain boundary effects) is unfortunately not feasible for the project size, \$, and scope.

Collaboration and Coordination With other Institutions

- **Bruce Davis, VP Technology, Magnesium Elektron North America**
 - In-kind cost share partner for manufacture of model and commercial alloys, conversion coatings (\$210k planned total cost share)
 - Ongoing role with experimental planning and interpretation
 - Additional coating participation via MENA industrial partners
- **Mostafa Fayek, Canada Research Chair in Isotope & Environmental Geochemistry, University of Manitoba**
 - SIMS analysis for tracer studies of Mg film growth mechanism (unique capabilities and expertise from geochemical systems)
 - Longtime collaborator with ORNL geochemistry and materials science
- **Joey Kish, Associate Professor, Materials Science and Engineering, McMaster University**
 - One of leading groups pursuing TEM studies of Mg corrosion
 - Ongoing informal collaborations/discussions of methods and results

Future Work

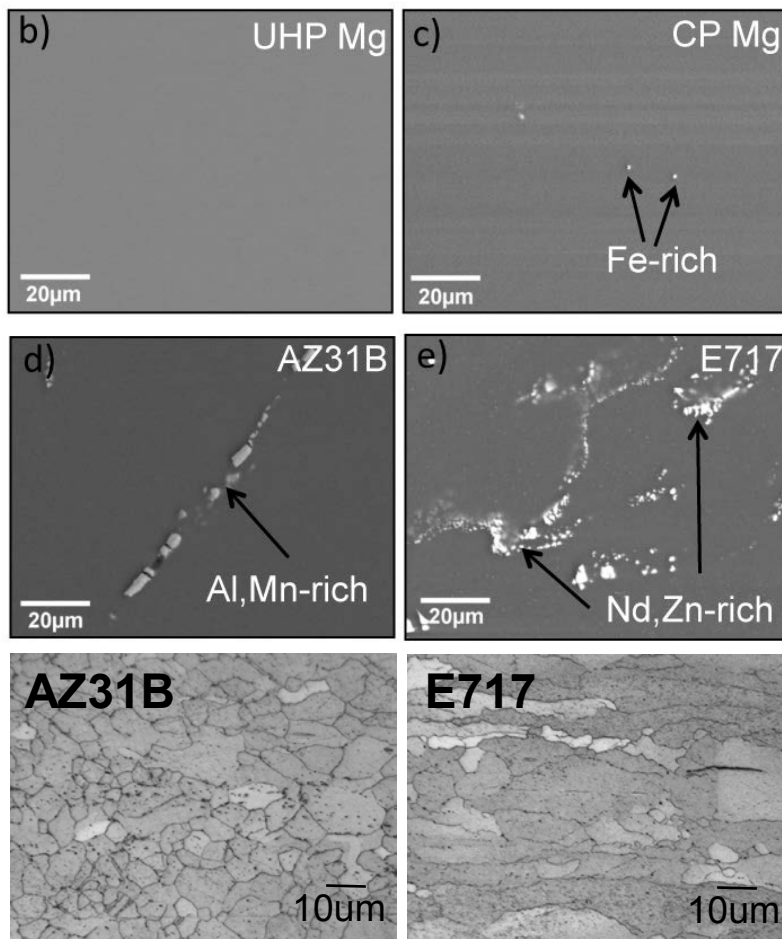
- Complete TEM and SANS characterization of film formation for E717 and AZ31B in water + salt (FY 14 paper milestone)
- Water and water + salt immersion and electrochemical studies of model E717 alloys \pm Zn \pm Nd/Ce to better delineate role and importance of rare earth, Zr, Zn on film nanostructure (TEM, XPS)
- Expanded SIMS isotopic tracer study activities:
 - TEM + water tracer studies for model E717 alloys \pm Zn \pm Nd/Ce to better understand increased H/D uptake observed for E717
 - attempt tracer study for UHP Mg, AZ31B, and E717 in water + salt
- TEM, XPS, SANS studies of Alodine® 5200 (benchmark) and Surtech® 650 (Cr, not +6) \pm BASF 525 E-coat of AZ31B and E717 to compare with bare metal film formation
 - as-coated
 - immersion exposures in water \pm NaCl
 - electrochemical studies in water \pm NaCl

Summary: Techniques Yielding New Film Insights

- ✓ Successful demonstration of SIMS/tracer approach for Mg in water
 - inward film growth by alloys vs. likely mixed film growth by pure Mg
 - extensive inward short circuit H/D penetration in film + metal by E717
 - H/D uptake in metal underlying film for UHP Mg, AZ31B, and E717
(implications not only for films but also for SCC, hydrogen storage, etc.)
- ✓ TEM: Alloy segregation in films for 1% NaCl different than in H₂O
 - Al in AZ31B and Zn₂Zr₃ nano precipitates in E717 films limited to inner MgO layer, not observed in thick outer Mg(OH)₂ in NaCl
 - Cl penetrates to inner MgO film, Zn segregation lessened at film-metal interface
- ✓ SANS useful to quantify outer porous Mg(OH)₂ films in salt
 - D₂O + NaCl to enhance film scattering, similar for AZ31B and E717
 - H₂O/D₂O (no NaCl) little film scattering: nanoporosity and potential preferential H/D segregation below detection limit in water-formed films

Technical Back-Up Slides

Initial Alloy Characterization



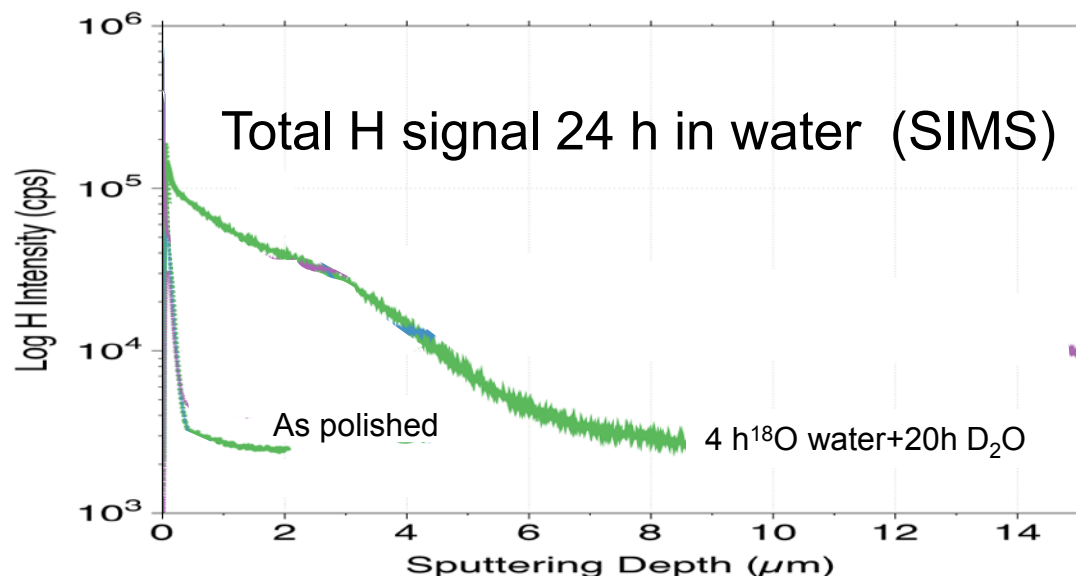
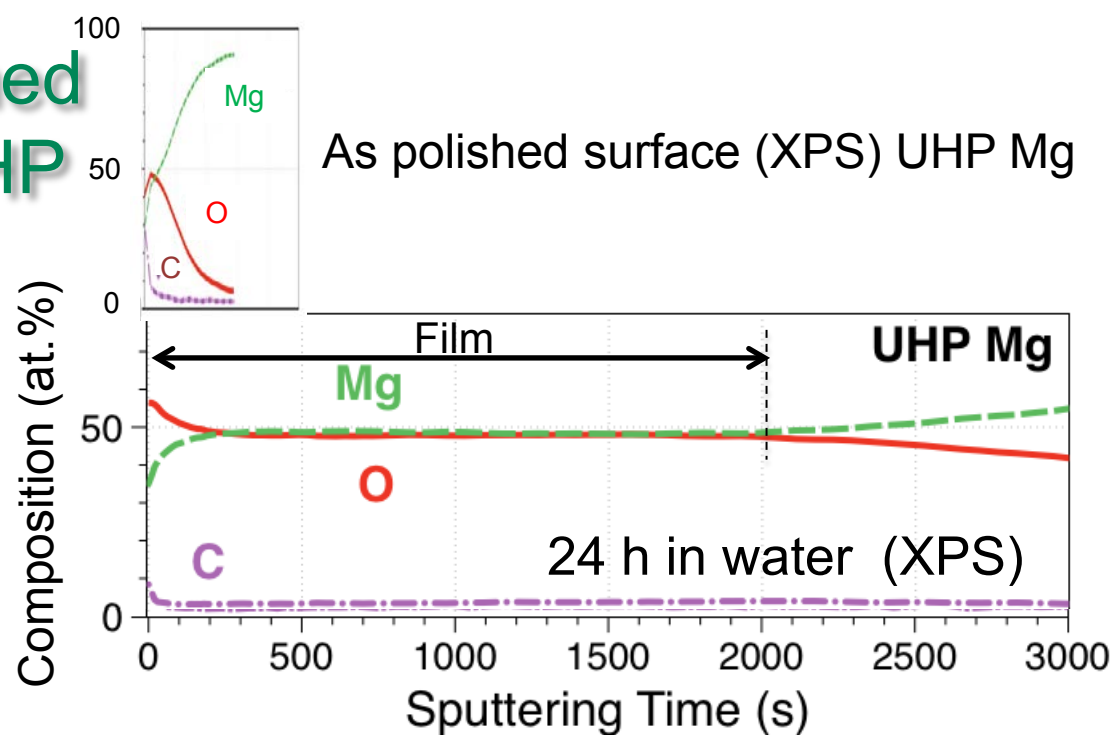
- Mainly single phase with small amounts of intermetallics
- Alloy grain sizes much smaller than UHP Mg (> 1mm grains)
- As-prepared control surfaces characterized by XPS and SIMS

UHP Mg: ~20 wppm Fe
CP Mg: ~80 wppm Fe

AZ31B: ~60 wppm Fe
E717: ~40 wppm Fe

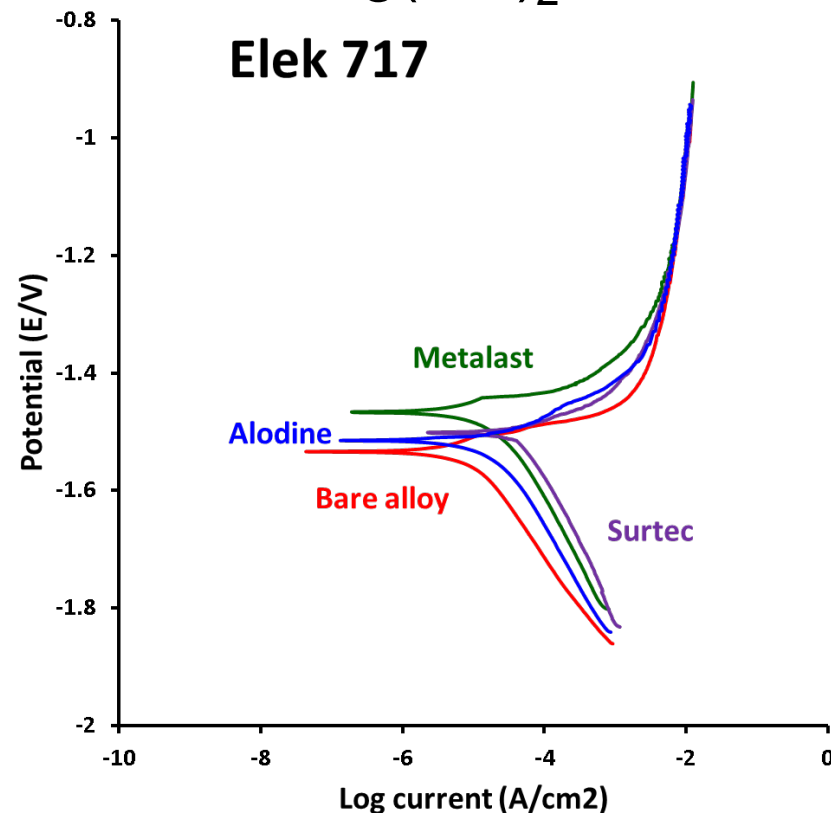
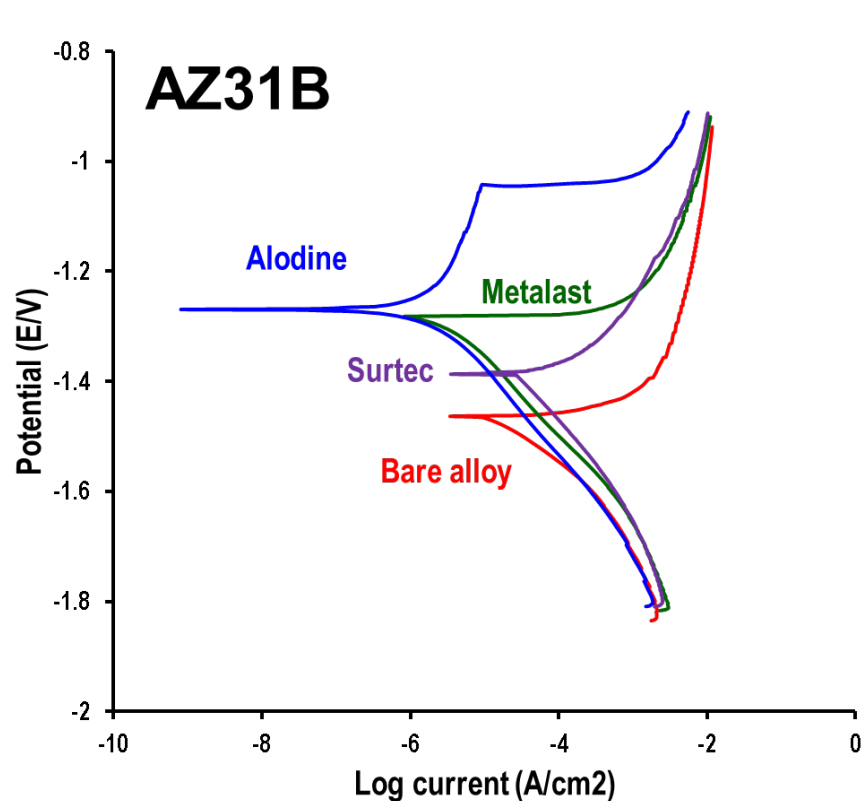
Typical Water-Formed Film: Shown for UHP Mg

- Film mainly MgO , partially hydrated
- $\text{Mg}(\text{OH})_2$, MgCO_3 also at outer surface



Potentiodynamic Polarization Data for Bare and As-Conversion Coated AZ31B and E717

Water + 1 wt.% NaCl Saturated with $\text{Mg}(\text{OH})_2$

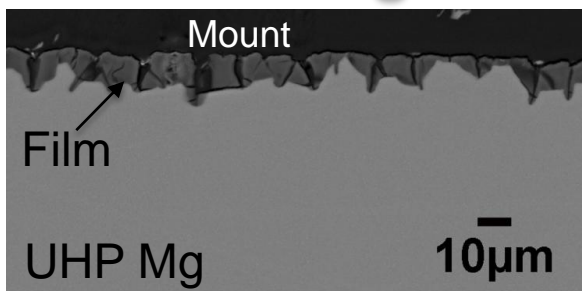


- Same source alloy/coating batches as SANS, XPS, and TEM studies
- Conversion coatings + BASF 525 E-coat in FY 15

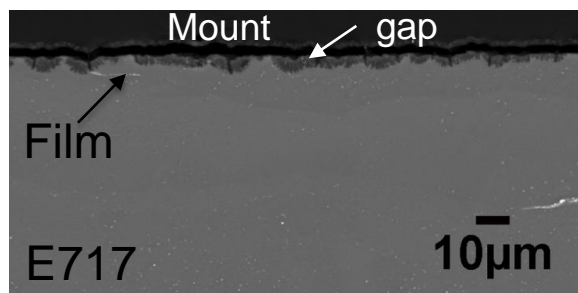
Non-Uniform, Cracked Film Formed after 24-48 h in Water (cracks not at alloy grain boundaries)

48h in DI water (polished)

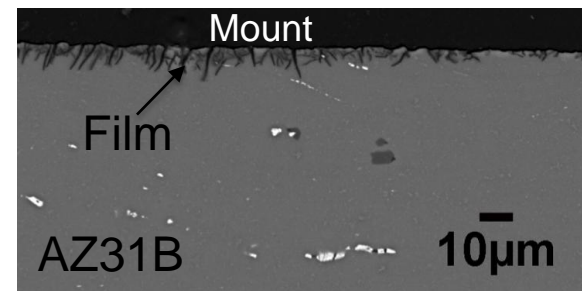
UHP Mg



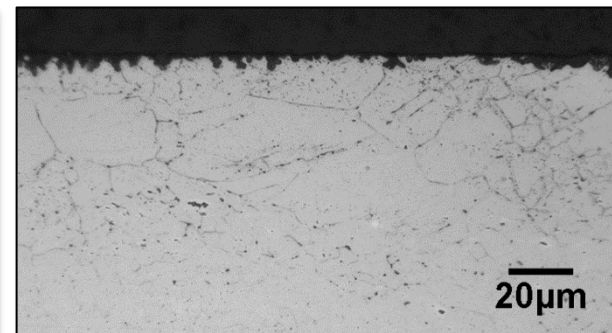
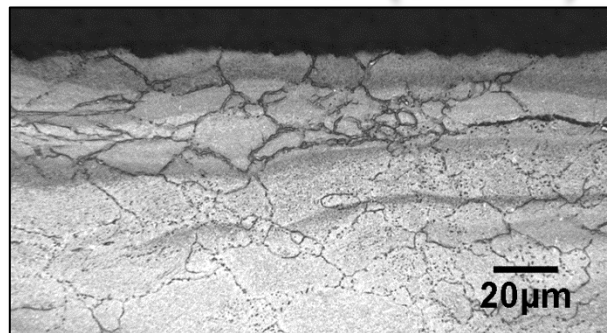
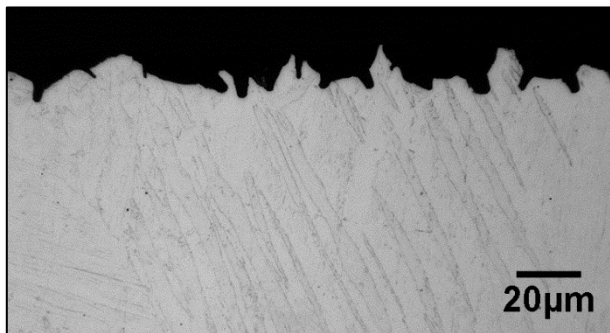
E717



AZ31B

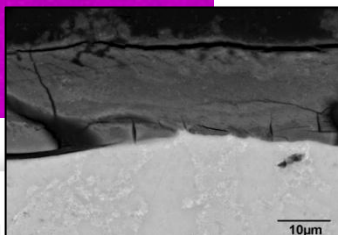
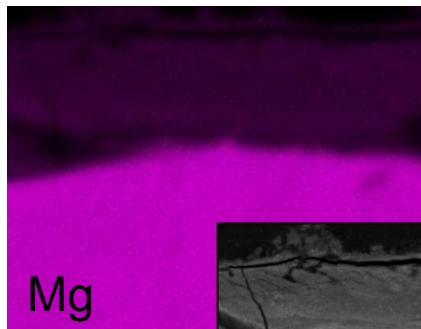
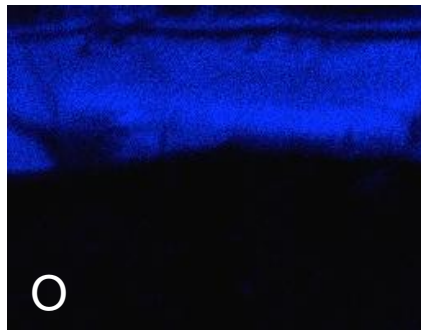
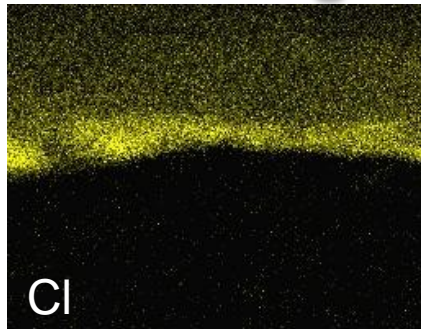


48h in DI water (etched)

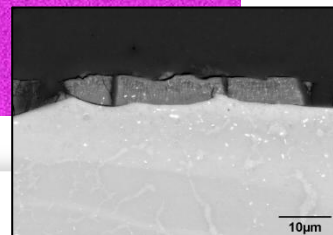
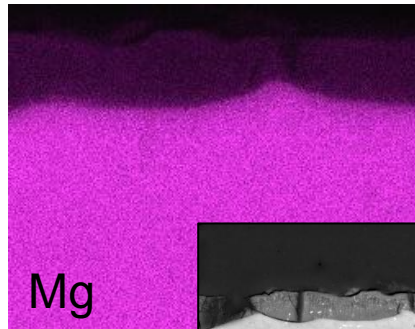
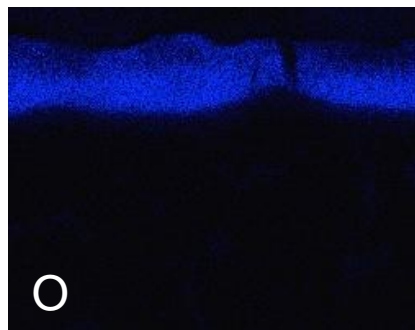
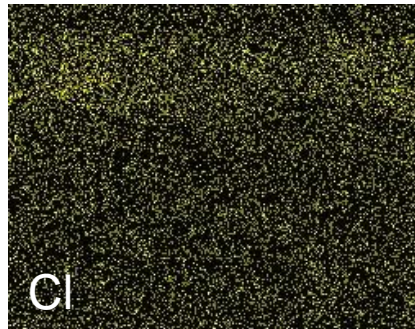


Cl Found in Film Inner Layer in Both UHP Mg and AZ31B (not E717) After 48h in 1%NaCl

UHP Mg



E717



AZ31B

